# Fabrication and Degradation of Polyperoxides by a Radical Chain Process under Mild Conditions

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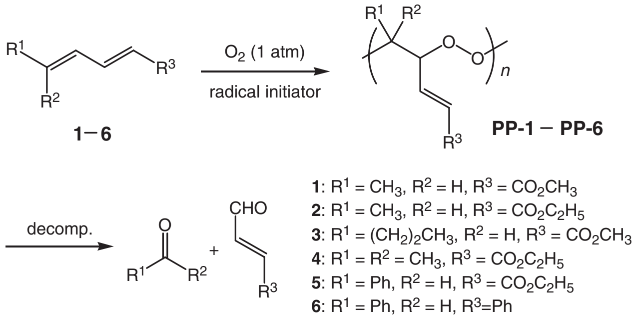
We have fabricated polyperoxides as new kinds of environment-friendly and degradable polymers using 1,3-diene compounds and oxygen as the starting comonomers under mild temperature and pressure conditions. They degrade in a radical chain mechanism by various stimuli; for example, degradation induced by physical (heating or irradiation), chemical (redox), and biochemical (enzymatic) stimuli.

Degradable polymers attract great interest owing to their versatile functions and applications, but very few kinds of vinyl polymers are feasible for use as degradable materials.[1] This is due to the fact that vinyl polymers have successive carbon-to-carbon bonds in the main chain, leading to their advantageous thermal and biochemical stabilities during processing and long-term use in daily life. Staudinger[2] first pointed out the formation of polyperoxides via the oxidation of vinyl monomers in 1922, and thereafter many kinds of polyperoxides have been prepared by a radical copolymerization process.[3–5] All polyperoxides obtained from vinyl monomers with oxygen readily decompose upon heating and provide formaldehyde as well as other aldehydes or ketones, according to the polymer repeating structure. In order to avoid the evolution of volatile and toxic compounds as the decomposition products, we have recently developed the synthesis of polyperoxides from diene monomers as a new kind of environment-friendly and degradable polymer. Here we report the preparation of polyperoxides from 1,3-diene monomers with oxygen and their degradation behavior by various stimuli; for example, degradation induced by physical (heating or irradiation), chemical (redox), and biochemical (enzymatic) stimuli. Both the fabrication and degradation processes of the polyperoxides imply efficient radical chain reactions.



**1**: $R^1 = CH_3$, $R^2 = H$, $R^3 = CO_2CH_3$
**2**: $R^1 = CH_3$, $R^2 = H$, $R^3 = CO_2C_2H_5$
**3**: $R^1 = (CH_2)_2CH_3$, $R^2 = H$, $R^3 = CO_2CH_3$
**4**: $R^1 = R^2 = CH_3$, $R^3 = CO_2C_2H_5$
**5**: $R^1 = Ph$, $R^2 = H$, $R^3 = CO_2C_2H_5$
**6**: $R^1 = Ph$, $R^2 = H$, $R^3 = Ph$

**Scheme 1.**

We have previously revealed that polyperoxides are obtained by the radical copolymerization of 1,3-diene monomers such as alkyl sorbates with oxygen as the starting monomers under mild polymerization conditions (ambient pressure and temperature).[6] They produce acetaldehyde as the decomposition product in lieu of formaldehyde produced from the polyperoxides that was derived from vinyl monomers. In this study, we have confirmed that the introduction of alkyl or phenyl substituents on a diene moiety leads to a change in the structure of the decomposition products, as shown in Scheme 1. Radical copolymerization of 1,3-diene monomers with oxygen was carried out in an organic solvent such as 1,2-dichloroethane in the presence of 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) as an azo initiator and bubbling oxygen at 30 °C and atmospheric pressure. The results of the polymerization as well as the thermal properties of the resulting polyperoxides are summarized in Table 1. The polymer yield decreased with an increase in the steric hindrance of the substituent on the diene monomers. All the polymers have a molecular weight of 2–4 × $10^3$. The decomposition temperature was estimated by thermogravimetric analy-

**Table 1.** Preparation and thermal properties of polyperoxides

| Poly-peroxide | Preparation[a] | | | TG[b] | | | DTA[b] | | | Degradation Products[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| | Yield/% | $M_n \times 10^{-3}$ | $M_w/M_n$ | $T_{95}$/°C | $T_{50}$/°C | $T_{max}$/°C | $T_{init}$/°C | $T_{max}$/°C | $\Delta H$/kJ unit$^{-1}$ | |
| **PP-1** | 49.3 | 3.9 | 1.6 | 119.5 | 149.8 | 148.2 | 107.9 | 147.5 | 187.3 | AcA + FA |
| **PP-2** | 39.1 | 4.0 | 1.8 | 122.3 | 149.9 | 145.3 | 107.4 | 147.0 | 187.6 | AcA + FA |
| **PP-3** | 21.6 | 3.1 | 1.4 | 115.1 | 146.1 | 141.3 | 88.5 | 140.7 | 165.7 | BuA + FA |
| **PP-4** | 28.9 | 4.4 | 1.5 | 104.8 | 132.2 | 129.6 | 82.3 | 128.6 | 166.7 | acetone + FA |
| **PP-5** | 14.6 | 2.3 | 2.1 | 105.6 | 154.5 | 129.4 | 72.0 | 120.5 | 162.9 | BzA + FA + EG + CA |
| **PP-6** | 21.9 | 2.9 | 2.1 | 102.9 | 133.6 | 117.5 | 76.1 | 109.5 | 175.7 | BzA + CA |

[a] Polymerization conditions: With bubbling oxygen for 6 h. Monomer/solvent = 1/1 in weight, except 1/13 for the polymerization of **6**. Monomer/AMVN = 50/1 in weight. The number-average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) were determined by GPC calibrated with standard polystyrenes. [b] Heating rate at 10 °C/min in a nitrogen stream. $T_{95}$ and $T_{50}$ are 95 and 50 wt % temperatures, respectively. $T_{init}$ and $T_{max}$ were determined from a differential TG or DTA curve. $\Delta H$ is the heat of decomposition. [c] Determined by NMR spectroscopy. AcA: acetaldehyde, FA: fumaraldehyde monoester, BuA: butylaldehyde, BzA: benzaldehyde, EG: ethyl glyoxylate, CA: cinnamaldehyde.

**Table 2.** Degradation of **PP-4** under various conditions

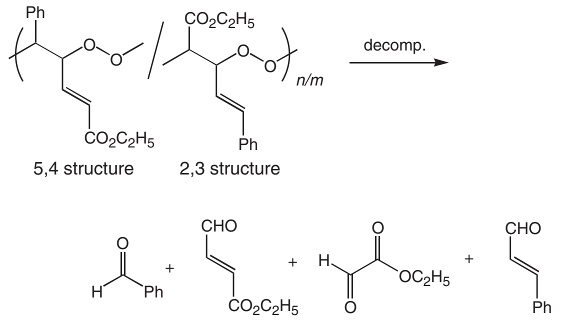
| Degradation Conditions | | | | Conv. | Product yield/% |
|---|---|---|---|---|---|
| Temp /°C | Time /h | Solvent | Additive | /% | Acetone/FA (ratio) |
| 90 | 1 | toluene-$d_8$ | none | 45.8 | 52.6/49.0 (1/0.93) |
| 90 | 2 | toluene-$d_8$ | none | 78.7 | 76.0/63.4 (1/0.83) |
| 90 | 3 | toluene-$d_8$ | none | 88.1 | 87.8/69.6 (1/0.79) |
| 90 | 5 | toluene-$d_8$ | none | 97.8 | 83.0/64.8 (1/0.78) |
| 110 | 0.5 | toluene-$d_8$ | none | 91.0 | 85.8/81.6 (1/0.95) |
| 30 ($h\nu$) | 3 | toluene-$d_8$ | none | 42.5 | 53.4/36.2 (1/0.68) |
| 30 ($h\nu$) | 12 | toluene-$d_8$ | none | 81.8 | 85.0/26.0 (1/0.31) |
| r.t. | 0.5 | benzene-$d_6$ | $NEt_3$[a] | ≈100 | [b] |
| 30 | 3 days | ethanol-$d_6$ | HRP[c] | 45.7 | [b] |

[a] $NEt_3$, 0.24 mol/L. [b] Not determined. [c] **PP-4** 25 mg, HRP 1.25 mg.

sis (TG) and differential thermal analysis (DTA) in a nitrogen stream at a heating rate of 10 °C/min. It was confirmed that the polyperoxides readily and exothermically decompose upon heating ($\Delta H = 163$–$188$ kJ/unit). The onset temperatures of the decomposition ($T_{\rm init}$) were 72–89 °C for **PP-3**–**PP-6**, being lower than those for the polyperoxides obtained from sorbates. The maximum decomposition temperature ($T_{\rm max}$) also showed similar results. The TG and DTA experiments support their thermal stability depending on the structure of the $R^1$ and $R^2$ substituents on the polymer main chain.

In order to determine the decomposition products, the polyperoxides in toluene-$d_8$ in a sealed tube were heated, and the decomposition products were examined as a reaction mixture by NMR spectroscopy. A fumaraldehyde monoester was produced from all the polyperoxides with an alkoxycarbonyl group as $R^3$, and acetaldehyde, butyladehyde, acetone, and benzaldehyde were also detected as another decomposition product from **PP-1** (or **PP-2**), **PP-3**, **PP-4**, and **PP-5**, respectively, as expected. As the decomposition products from **PP-5**, two further compounds, cinnamaldehyde and ethyl glyoxylate, were simultaneously found (Scheme 2). The NMR spectrum of **PP-5** suggested the existence of the 5,4 and 2,3 structures as the repeating unit in a 2:3 molar ratio. The presence of phenyl and carboxylate groups leads to attack of a peroxy radical at both the 2- and 5-positions and the subsequent cross propagation results in the polymer structure. Nevertheless, the degradation behavior was the same as that for the other polyperoxides except for four kinds of decomposition products. The decomposition products from **PP-5** consist of compounds with a high boiling point (low vapor pressure at room temperature) and less toxicity, compared to the decomposition products from polyperoxides derived from sorbates or vinyl monomers. **PP-6** provided the most simple and environmentally friendly decomposition products, i.e., benzaldehyde and cinnamaldehyde.

The degradation reaction proceeds via a radical chain reaction mechanism.[3b,4] A peroxy bond in the polymer chain is homolitically cleaved during the first step, followed by the successive $\beta$-scission (also via a radical chain reaction) providing two kinds of aldehydes alternately. These polyperoxides degrade not only upon heating but also by other stimuli. For example, photochemical or redox reactions are available for decomposition at ambient temperature, as well as an enzymatic trigger such as *Horseradish Peroxidase* (HRP) (Table 2). During photoirradiation, the fumaraldehyde monoesters produced by the decomposition of the polyperoxide further reacted via EZ isomerization, dimerization, and other reactions, leading to a low fumaraldehyde to acetone ratio. The addition of a basic compound, such as triethylamine, induced a rapid decomposition accompanying by complicated reaction products. The biochemical decomposition of the polyperoxides by HRP also proceeds via a radical chain reaction mechanism, providing similar main products during decomposition. The polymers degradable via a radical chain reaction mechanism triggered by various stimuli have a potential for use in various fields including adhesion, coating, environmental, and medicinal chemistry.



**Scheme 2.**

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